

What is claimed is:

1. A positive-working photoresist comprising:

(A) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight ( $M_n$ ) of at least 1000; and

(B) at least one photoacid generator.

2. The photoresist of Claim 1 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

3. The photoresist of Claim 2 wherein the branch segment(s) contains greater than 50% of the protected acid groups present in the branched polymer.

4. The photoresist of Claim 1 wherein the branched polymer contains functional groups that are compatible with the photoacid generator, said functional groups being distributed in the branched polymer such that 25 to 100% of the functional groups are present in the segment of the branched polymer containing a majority of the protected acid groups.

5. The photoresist of Claim 1 wherein the photoacid generator is covalently bonded to the branched polymer.

6. The photoresist of Claim 5 wherein the photoacid generator is covalently bonded to the branch segment(s).

7. The photoresist of Claim 6 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

8. The photoresist of Claim 7 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

9. The photoresist of Claim 1 wherein the branched polymer is comprised of an acrylate polymer, a methacrylate polymer, an acrylate/methacrylate copolymer, and combinations thereof.

10. The photoresist of Claim 1 further comprising a solvent.

11. The photoresist of Claim 1 wherein the branched polymer is formed by addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer.

12. The photoresist of Claim 1 wherein the branched polymer segment is attached to a preformed linear backbone by chemical reaction.

13. The photoresist of Claim 11 wherein

(a) the ethylenically unsaturated macromonomer component has a number average molecular weight ( $M_n$ ) in the range of 1000 to 15,000;

3 (b) the linear backbone segment has a number average molecular weight ( $M_n$ ) between 2,000 and 500,000; and

(c) the weight ratio of the linear backbone segment to the branch segment(s) is within a range of 50/1 to 1/10.

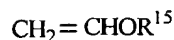
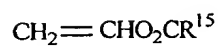
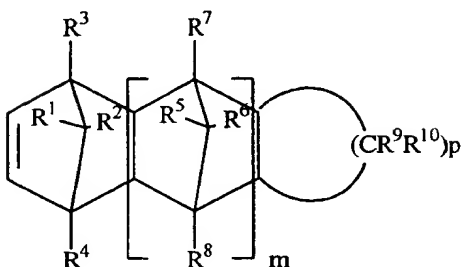
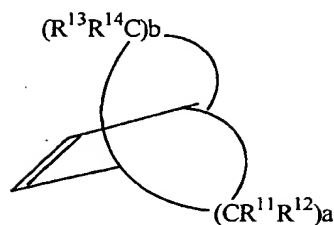
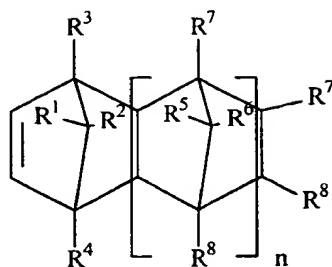
14. The photoresist of Claim 1 wherein the branched polymer has a glass transition temperature of at least 22°C.

10 15. The photoresist of Claim 1 further comprising a dissolution inhibitor.

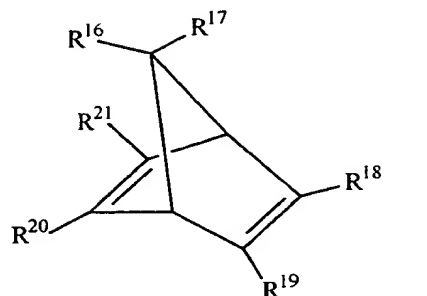
16. The photoresist of Claim 1 wherein the branched polymer is an acrylic/methacrylic/styrenic copolymer being at least 60% by weight acrylate and having at least 60% of methacrylate repeat units present either in a first location or a second location, the first location being one of the segments, the second location being a segment different from the first location, wherein at least 60% of the acrylate repeat units are present in the second location.

15 17. The photoresist of Claim 1 wherein the branched polymer is a fluorine-containing copolymer comprising a <sup>repeat</sup> repeat unit derived from at least one ethylenically unsaturated compound containing at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom.

20 18. The photoresist of Claim 17 wherein the fluorine-containing copolymer is further comprised of a repeat unit derived from at least one unsaturated compound selected from the group consisting of:



and



wherein:

each of m and n is 0, 1 or 2, p is an integer of at least 3;

5 a and b are independently 1 to 3 except that a is not = 1 when b = 2 or vice versa;

R<sup>1</sup> to R<sup>14</sup> are the same or different and each represents a hydrogen atom, a halogen atom, a carboxyl group, a C<sub>1</sub> to C<sub>14</sub> secondary or tertiary alkyl carboxylate, a hydrocarbon group or a substituted hydrocarbon group;

10 R<sup>15</sup> is a saturated alkyl group of about 4 to 20 carbon atoms, optionally containing one or more ether oxygens with the proviso that the ratio of carbon atoms to hydrogen atoms is greater than or equal to 0.58; and

R<sup>16</sup> to R<sup>21</sup> are each independently hydrogen atoms, C<sub>1</sub> to C<sub>12</sub> alkyls, (CH<sub>2</sub>)<sub>q</sub>CO<sub>2</sub>A, CO<sub>2</sub>(CH<sub>2</sub>)<sub>q</sub>CO<sub>2</sub>A or CO<sub>2</sub>A wherein q is 1 to 12 and A is hydrogen

or an acid protecting group with the proviso that at least one of R<sup>18</sup> to R<sup>21</sup> is CO<sub>2</sub>A.

19. The photoresist of Claim 18 wherein the fluorine-containing copolymer further comprises a repeat unit derived from at least one ethylenically unsaturated compound containing a fluoroalcohol functional group having the structure:



- wherein R<sub>f</sub> and R<sub>f</sub>' are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are (CF<sub>2</sub>)<sub>n</sub> wherein n is 2 to 10.

20. The photoresist of Claim 17 wherein the fluorine-containing copolymer further comprises a repeat unit derived from at least one ethylenically unsaturated compound containing a fluoroalcohol functional group having the structure:



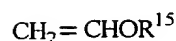
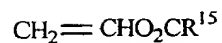
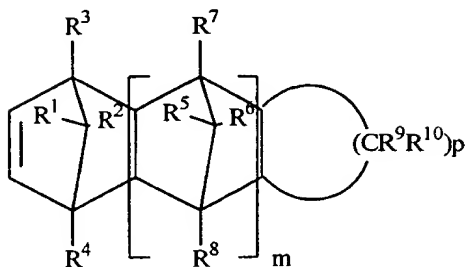
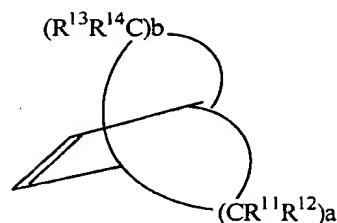
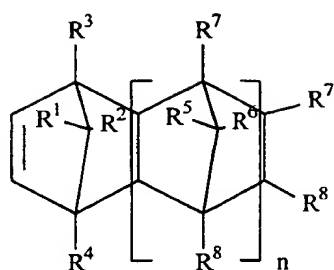
- wherein R<sub>f</sub> and R<sub>f</sub>' are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are (CF<sub>2</sub>)<sub>n</sub> wherein n is 2 to 10.

21. The photoresist of Claim 1 wherein the branched polymer is a fluorine-containing copolymer comprising a repeat unit derived from at least one ethylenically unsaturated compound containing a fluoroalcohol functional group having the structure:

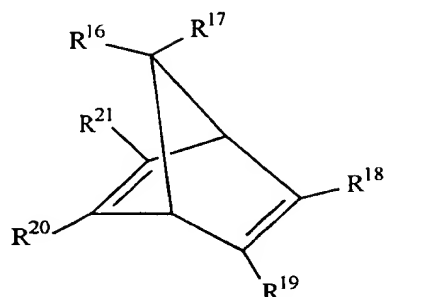


- wherein R<sub>f</sub> and R<sub>f</sub>' are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are (CF<sub>2</sub>)<sub>n</sub> wherein n is 2 to 10.

22. The photoresist of Claim 21 wherein the fluorine-containing copolymer is further comprised of a repeat unit derived from at least one unsaturated compound selected from the group consisting of:



and



wherein:

each of  $m$  and  $n$  is 0, 1 or 2,  $p$  is an integer of at least 3;

$a$  and  $b$  are independently 1 to 3 except that  $a$  is not = 1 when  $b = 2$  or vice versa;

5  $\text{R}^1$  to  $\text{R}^{14}$  are the same or different and each represents a hydrogen atom, a halogen atom, a carboxyl group, a  $\text{C}_1$  to  $\text{C}_{14}$  secondary or tertiary alkyl carboxylate, a hydrocarbon group or a substituted hydrocarbon group;

$\text{R}^{15}$  is a saturated alkyl group of about 4 to 20 carbon atoms, optionally containing one or more ether oxygens with the proviso that the ratio of  
10 carbon atoms to hydrogen atoms is greater than or equal to 0.58; and

$\text{R}^{16}$  to  $\text{R}^{21}$  are each independently hydrogen atoms,  $\text{C}_1$  to  $\text{C}_{12}$  alkyls,  $(\text{CH}_2)_q\text{CO}_2\text{A}$ ,  $\text{CO}_2(\text{CH}_2)_q\text{CO}_2\text{A}$  or  $\text{CO}_2\text{A}$  wherein  $q$  is 1 to 12 and  $\text{A}$  is hydrogen or an acid protecting group with the proviso that at least one of  $\text{R}^{18}$  to  $\text{R}^{21}$  is  $\text{CO}_2\text{A}$ .

23. The photoresist of Claim 21 wherein the photoacid generator is covalently bonded to the branched polymer.

24. The photoresist of Claim 23 wherein the photoacid generator is covalently bonded to the branch segment(s).

5 25. The photoresist of Claim 24 wherein one of the segments contains greater than 50% of the protected acid groups present in the branched polymer.

26. The photoresist of Claim 25 wherein the branch segment(s) contain greater than 50% of the protected acid groups present in the branched polymer.

10 27. A process for preparing a photoresist image on a substrate comprising, in order:

(W) applying a photoresist composition on a substrate, wherein the photoresist composition comprises:

15 (a) a branched polymer containing protected acid groups, said polymer comprising one or more branch segment(s) chemically linked along a linear backbone segment, wherein the branched polymer contains sufficient functionality to render the photoresist developable to afford a relief image, upon imagewise exposure to radiation selected from the group consisting of ultraviolet and violet and subsequent heating, and wherein the branch segment(s) contain at least two repeating monomer units and have a number average molecular weight  
20 ( $M_n$ ) of at least 1000;

(b) at least one photoacid generator; and

(c) a solvent;

(X) drying the coated photoresist composition to remove solvent and thereby to form a photoresist layer on the substrate;

25 (Y) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(Z) developing the exposed photoresist layer having images and non-imaged areas to form the relief image on the substrate.

30 28. The process of Claim 27 further comprising a step of heating the photoresist layer following step (X) and prior to step (Z).

29. The process of Claim 27 wherein the photoresist layer is developed with an aqueous alkaline developer.

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